

PATENT SPECIFICATION

631590



Application Date: May 24, 1946.

No. 15794/46.

Complete Specification Accepted: Nov. 7, 1949.

Index at acceptance:—Class 2(v), R4c(2: 5: 6: 9: 10: 12: 14: 16), R4(d5: m2: t2), R18c(2: 5: 6: 9: 10: 12: 14: 16), R18(m: p: t2), R25c(2: 5: 6: 9: 10: 12: 14: 16), R25(m: p: t2).

COMPLETE SPECIFICATION

Improved Synthetic Resins

We, E. I. DU PONT DE NEMOURS and Co., a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, DONALD DRAKE COFFMAN and HENNING WALDEMAR JACOBSON, citizens of the United States of America, of 111, South Road, Lindamere, and 303 N Maryland Avenue, Richardson Park, respectively, Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improved synthetic resins, particularly heat-hardenable resins. The low cost of ethylene has stimulated the preparation and characterisation of a wide variety of ethylene interpolymers. Three component interpolymers of ethylene with vinyl esters and esters of unsaturated dibasic acids are known, but in common with certain other ethylene interpolymers these are soft, low-melting products with poor resistance to organic solvents and cannot be hardened by mild heat treatment. These properties are distinctly disadvantageous in applications such as moulded articles, fibres, tubes and other uses in which a combination of high softening temperature and insolubility is desired.

An object of the present invention is to provide a process for the production of heat-hardenable, interpolymer resins. Another object is to provide a process for the production from ethylene, vinyl acetate and fumaric esters, of resins that may be cured by heat treatment to give insoluble, high-softening, moulded products. Other objects and advantages of the invention will appear hereinafter.

According to the present invention these objects are accomplished by a process which comprises the step of hydrolysing ethylene/vinyl acetate/fumaric ester interpolymers, said fumaric esters being diesters of aliphatic alcohols containing

not more than four carbon atoms.

By varying the ratio of ethylene to vinyl acetate to fumaric ester in the polymerisation charge, a wide variety of ethylene/vinyl acetate/fumaric ester interpolymers can be obtained. These products, in turn, on hydrolysis give products which show a great variation in properties depending on the mole ratio of the polymer constituents in the unhydrolysed polymer. Hydrolysed products made from interpolymers with a high ratio of ethylene to vinyl acetate and fumaric ester, such as 25:2:1, are soft and pliable. On heating such hydrolysed interpolymers they become insoluble and higher softening but retain their soft, pliable characteristics. Polymers wherein the mole ratio of vinyl acetate to fumaric ester is 2/1 but wherein the mole ratio of ethylene is much lower than in those described above, as for example 4:2:1, are generally quite hard and brittle and heat treatment of the hydrolysed interpolymer causes complete insolubilisation. The preferred hydrolysed ethylene/vinyl acetate/fumaric ester interpolymers are those made from interpolymers wherein the mol ratio of ethylene to vinyl acetate is at least 1:1 and of vinyl acetate to fumaric ester greater than 2:1. Those made from interpolymers wherein the ratio of ethylene to vinyl acetate is at least 1:1 but less than 12:1 and the mole ratio of vinyl acetate to fumaric ester is between 2:1 and 50:1 and preferably less than 30:1 are further preferred. Hydrolysed products from interpolymers in this range, as for example 1.8:1:0.07, are tough and pliable and give excellent filled mouldings, films and fibres. Diethyl fumarate is the preferred fumaric ester used in the preparation of the interpolymers, on account of its availability and low cost.

Three component interpolymers of ethylene, vinyl acetate and fumaric esters are prepared by heating the constituents to a temperature above 40° C. under superatmospheric pressure in bulk, solu-

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tion or emulsion with a dissolved or suspended vinyl polymerisation catalyst. The general method of operation is described in co-pending British Application No. 9091/43 (Serial No. 582,093).

The ethylene used in the preparation of the interpolymers may be from any source, but for the best results it should be purified before use. Low proportions of methane, ethane, nitrogen, hydrogen and oxygen may be tolerated. Because ethylene polymerisations in general are effected by the concentration of oxygen present, this substance should be low in concentration and preferably below 50 p.p.m. for ease of interpolymerisation.

The vinyl acetate and fumaric ester used in the preparation of the interpolymers for the practice of this invention should be of a good grade and are generally distilled prior to use to remove inhibitors and impurities.

The temperature employed in the polymerisation step may be from 40°—300° C., but it is preferred to keep the temperature at about 65° C. for at this temperature a sufficiently rapid and easily controlled reaction is obtained.

The pressures employed for interpolymer preparation may vary from 60 to 1000 atms. of ethylene and upwards depending chiefly on the strength of the equipment. The higher pressures, e.g. 840—1000 atmospheres, are preferable since under these conditions products of higher molecular weight are obtained.

Catalysts useful for the preparation of ethylene/vinyl acetate/ fumaric ester interpolymers are those known to induce the polymerisation of ethylene and include oxygen at low concentrations, organic peroxy compounds of the class of diacyl peroxides such as benzoyl peroxide, dialkyl peroxides such as diethyl dioxide, and alkyl hydroperoxides such as tertiary butyl hydroperoxide, perchloro compounds such as hexachloroethane, salts of halogenated aromatic sulphonamides such as Chloramine T, hydrazine derivatives such as dibenzoyl hydrazine and other agents capable of liberating free radicals.

Agitation is preferred for the interpolymerisations which may be carried out batchwise, semicontinuously or continuously in equipment capable of withstanding the pressures developed. It is preferable to have that portion of the equipment which comes in direct contact with reactants and the interpolymers lined with a material which will not corrode or influence the course of the polymerisation. Suitable materials include silver, aluminium, tin, glass, stainless steel, "Monel Metal" (Registered Trade

Mark) and nickel.

The following procedure will illustrate a suitable general method of preparing ethylene/vinyl acetate/fumaric ester interpolymers.

A pressure vessel is charged with vinyl acetate and fumaric ester in approximate amounts desired in the final interpolymer and a vinyl polymerisation catalyst such as benzoyl peroxide. The vessel is closed, placed in a shaking machine provided with a heater, and is connected with a source of ethylene under pressure. Temperature recording and controlling thermocouples are inserted, and heating and agitation are begun. When a temperature of 50°—150° C. is recorded, the pressure is adjusted to between 60 and 1500 atmospheres of ethylene pressure. After a brief induction period reaction begins and the pressure drops due to the interpolymerisation of ethylene. The reaction is carried out in the desired pressure range by periodic repressuring with ethylene. At the end of the polymerisation, as evidenced by cessation of pressure drop, the pressure vessel is cooled, bled of unreacted gases, opened, and discharged. The interpolymer is generally freed of vinyl acetate and fumaric ester by steam distillation and is dried under reduced pressure.

The hydrolysis is preferably carried out in a primary alcohol which is liquid at 25° C. or in a solvent mixture of which one component is such an alcohol in the amount of at least 25% by weight of said solvent mixture. The most suitable alcohols are methyl alcohol and ethyl alcohol, but higher alcohols such as propyl, butyl and isobutyl alcohol may also be used to advantage. In cases where the interpolymer is not sufficiently soluble in the alcohol used, the solubility of the interpolymer may be improved by the use of a mixed solvent consisting of alcohol together with another solvent such as benzene, toluene, xylene, pyridine, dioxane or trichlorethylene. In certain cases it may be desirable to carry out the hydrolysis in solvent systems containing appreciable amounts of water, as for example, in mixtures of water with acetic acid, dioxane, ethanol, methanol, or other water-miscible solvent. Alkaline conditions are preferably employed in carrying out the hydrolysis since under such conditions rapid and complete hydrolysis is effected. Since the unhydrolysed interpolymers are soluble in aromatic hydrocarbon solvents it is convenient to carry out the hydrolysis by adding an alcoholic solution of an alkali to a solution of the interpolymers in the

hydrocarbon. The hydrocarbon solution may also be diluted with the alcohol before addition of the alkali with good results. Benzene, toluene and xylene may be mentioned as examples of suitable solvents while methanol and ethanol serve well as diluents and solvents for the alkali which may be, for example, potassium hydroxide or sodium hydroxide. The temperature of hydrolysis may be varied depending upon the rapidity of hydrolysis desired but ordinarily the temperature used coincides with the reflux temperature of the particular solvent system used. The quantity of alkali added is not critical as long as an excess is used. Generally a 10% excess promotes a rapid and complete hydrolysis.

The following procedure will illustrate a suitable method of hydrolysis.

The interpolymer is dissolved in a suitable solvent, as for example, a mixture of an aromatic hydrocarbon such as benzene and an alcohol such as methanol. To the hot solution is added in excess an alcoholic solution of alkali such as potassium hydroxide in methanol. The resulting solution is refluxed for a period of 1 to 4 hours, at the end of which time the reaction mixture is poured into water containing hydrochloric acid in excess over that required to neutralise the alkali, and organic solvents are then conveniently removed by steam distillation. The hydrolysed interpolymers are generally not completely dried since this often leads to complete insolubilisation.

In making filled mouldings of hydrolysed ethylene/vinyl acetate/fumaric ester interpolymers the usual methods for incorporating fillers into resins may be employed, e.g. malaxating one or more fillers with the interpolymer or suspending the filler in a solution of the interpolymer followed by evaporation of the solvent. A variety of fillers such as asbestos, mica, carbon, cork, chalk or wood flour may be used. If coloured mouldings are desired suitable dyes and pigments may be added.

The moulding operation can be carried out over a range of temperature and pressure, but in general a 10—15 minute period under a pressure of 2000—3000 lb./sq. in. at a temperature of 150° C. is satisfactory. It would be expected that hydrolysed interpolymers containing an equivalent number of carboxyl and hydroxyl groups would lead to the highest tensile, impact, and flexural strengths but this is not the case. The preferred hydrolysed interpolymers, that is, hydrolysis products of interpolymers in which the mole ratio of ethylene to vinyl acetate is at least 1:1 and the mole

ratio of vinyl acetate to fumaric ester is greater than 2:1, give mouldings superior to products outside this range. This may readily be seen by comparing the properties of mouldings of a hydrolysed ethylene/vinyl acetate/diethyl fumarate of 1.8:1:0.07 mole ratio with one in which the mole ratio is 2.6:2:1 as shown in the appended table I.

TABLE I.

MOULDINGS OF HYDROLYSED ETHYLENE/VINYL ACETATE/FUMARIC ESTER INTERPOLYMERS.

Interpolymer.	Mol Ratio	Softening Pt. ° C.	Tensile Strength lbs./sq. in. % Elongation at break	Hardness (Rockwell M)	Stiffness (sag)	Flexural strength lbs./sq. in.	Impact strength (ft.lb./in.) notch
Hydrolysed ethylene/vinyl acetate/diethyl fumarate	1.8/1/0.07	160 150-up	5830/0 5000/0	60 90-120	1.21 0.6-0.8	9675 10000	0.54 0.35
Phenolic resin	-	-	-	-	-	-	-
Hydrolysed ethylene/vinyl acetate/diethyl fumarate	2.6/2/1	95	5620/0	54	1.08	9000	0.32

Methods of testing are described in the following publications.

Softening point co-pending British Application No. 5138/44.

Tensile Strength A.S.T.M. D-638-42T

Flexural Strength A.S.T.M. D-650-42T

Impact Strength A.S.T.M. D-256-41T

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Mouldings of both compositions contain 50% by weight of wood flour and were moulded at 2000 lb./sq. in. at 150° C. These resins are also compared with a phenolic resin.

Hydrolysed ethylene/vinyl acetate/fumaric ester interpolymers can be formed into films by methods such as solvent casting or hot pressing. Here again hydrolysed interpolymers in the preferred range are far superior to those outside this range as regards general film properties. Thus, a hydrolysed ethylene/vinyl acetate/diethyl fumarate interpolymer of mole ratio 1.8:1:0.07 is readily hot cast or pressed to films with a tensile strength of 2800 lb./sq. in. and an elongation of 40%. The softening point of the film is 120° C. and the temperature at which the tensile strength becomes zero is 112° C. By heating for 6 hours at 105° C., the softening point is increased to 200° C. and the zero tensile strength temperature is increased to 165° C. Hydrolysed products wherein the mole ratio of vinyl acetate to fumaric ester in the original interpolymer is not greater than 2:1 are hard, brittle, difficultly soluble in organic solvents and cannot be easily manipulated.

The following examples serve to illustrate the process of this invention but the invention is in no way limited by these Examples. Quantities given are expressed as parts by weight unless otherwise indicated.

EXAMPLE I.

(a) INTERPOLYMER PREPARATION

A silver-lined pressure vessel is charged with 150 parts of vinyl acetate, 17 parts of diethyl fumarate, and 0.3 parts of benzoyl peroxide. The vessel is closed, evacuated, and pressured with ethylene. Heating and agitation are begun and a temperature of 63°—67° C. maintained for a period of 10 hours during which time the ethylene pressure is maintained at 840—1000 atmospheres. When the pressure ceases to drop, indicating the end of the reaction, the vessel is cooled, bled of excess ethylene, opened and discharged. The interpolymer is freed of vinyl acetate and diethyl fumarate by steam distillation. There is obtained on drying 98 parts of tough, strong elastomeric ethylene / vinyl acetate/diethyl fumarate interpolymer which, as indicated in the section below has an ethylene/vinyl acetate/diethyl fumarate mole ratio of 1.8:1:0.07.

(b) INTERPOLYMER HYDROLYSIS

Forty-five parts of interpolymer, prepared as described above, are dissolved in 400 parts of benzene at reflux tempera-

ture with stirring. A solution of 30 parts of potassium hydroxide in 300 parts of methanol is added dropwise to the refluxing solution, and heating is continued for 4 hours. At the end of this time, the product is poured into a large volume of water containing 40 parts of concentrated hydrochloric acid. The hydrolysed interpolymer which separates is washed with water several times and sucked dry.

The original unhydrolysed interpolymer has a carbon content of 65.51%. By titration of the completely hydrolysed interpolymer in hot tertiary-butyl alcohol to the phenolphthalein end point it is found that 0.1710 gm. of polymer require 2.28 ml. of 0.1007 N sodium hydroxide for complete neutralisation. From this it may be calculated that the ethylene/vinyl acetate/diethyl fumarate mole ratio is 26.2:14.1:1 or 1.8:1:0.07.

(c) MOLDING OF HYDROLYSED INTERPOLYMER

Ten parts of hydrolysed interpolymer as obtained from the preceding step are dissolved in tertiary-butyl alcohol with stirring at reflux temperature and then 10 parts of wood flour are added. The solvent is removed by slow evaporation with good agitation. The homogeneous paste of interpolymer and wood flour thus formed is heated for a short period of time on the steam bath under reduced pressure to remove the remaining solvent, and is moulded at 150° C. under 2000 lb./sq. in. pressure for 10 minutes. These mouldings possess the following properties. Methods for testing are described in publications referred to in parenthesis and in Table I.

Softening Point—160° C.
Stiffness—1.21 mm. sag.
Hardness (Rockwell M)—60
Tensile Strength—5830 lb./sq. in.)
Elongation at Break Point—0%
(A.S.T.M. D—638—42T)
Impact Strength—0.540 ft. lb./in. notch
Flexural Strength—9675 lb./sq. in.

EXAMPLE II.

(a) INTERPOLYMER PREPARATION

A silver-lined pressure vessel is charged with 20 parts of vinyl acetate, 20 parts of diethyl fumarate, 100 parts of tertiary-butyl alcohol and 0.3 part of benzoyl peroxide. The vessel is closed, pressured with ethylene and is heated to a temperature of 64°—68° C. with good agitation. For the reaction period of 8.25 hours the ethylene pressure is maintained at 840—990 atmospheres and there is an observed pressure drop of 250 atmospheres. At the end of this time the pressure ceases to

drop and the vessel is cooled, bled of excess gas, opened and discharged. The product thus obtained is freed of solvent, excess vinyl acetate and diethyl fumarate by steam distillation. Upon drying 22 parts of a clear, strong elastomer containing 64.05% carbon are obtained, from which it may be calculated by assuming that the vinyl acetate and diethyl fumarate interpolymerise in the mole ratio in which they are charged (e.g. two moles vinyl acetate to one mole of diethyl fumarate), that the mole ratio of ethylene to vinyl acetate to diethyl fumarate is 4.7:2:1.

(b) INTERPOLYMER HYDROLYSIS

Twenty - two parts of the above-described interpolymer are dissolved in 250 parts of benzene at reflux with stirring and 75 parts of methanol are added followed by 25 parts of potassium hydroxide in 125 parts of methanol. The mixture is refluxed for about 4 hours and poured into 1000 parts of water containing 25 parts of concentrated hydrochloric acid. The precipitated hydrolysed ethylene/vinyl acetate/diethyl fumarate interpolymer of 4.7:2:1 mole ratio is steamed to remove benzene. During this procedure the substantially completely hydrolysed interpolymer shows a tendency to emulsify. It is precipitated by addition of sodium chloride after all benzene has been removed and is finally washed with cold water.

(c) MOULDING OF HYDROLYSED INTERPOLYMER

The hydrolysed interpolymer prepared as described above, is filled with wood flour and moulded as described in Example I. These mouldings are found to have the following properties by the methods referred to in Example I.

Softening Point—80° C.
Stiffness—1.56 mm.
Tensile Strength—3510 lb./sq. in.
Elongation at Break—5%
Impact Strength—0.480 ft. lb./in. of notch

Flexural Strength—6650 lb./sq. in.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of heat hardenable interpolymer resins which comprises the step of hydrolysing ethylene/vinyl acetate/fumaric ester interpolymers said fumaric esters being diesters of aliphatic alcohols containing not more than 4 carbon atoms.

2. A process according to claim 1

wherein the ethylene/vinyl acetate/fumaric ester interpolymer has an ethylene to vinyl acetate mol ratio of at least 1:1 and a vinyl acetate to fumaric ester mol ratio greater than 2:1.

3. A process according to claim 2 wherein the mole ratios of ethylene to vinyl acetate and of vinyl acetate to fumaric ester in the ethylene/vinyl acetate/fumaric ester interpolymer are less than 12:1 and less than 50:1 respectively.

4. A process according to claim 3 wherein the mole ratio of vinyl acetate to fumaric ester in the ethylene/vinyl acetate/fumaric ester interpolymer is less than 30:1.

5. A process according to claim 4 wherein the ethylene, vinyl acetate and fumaric ester of the interpolymer hydrolysed are in the mol ratio of 1.8:1.0:0.7.

6. A process according to any of the preceding claims wherein the fumaric ester is diethyl fumarate.

7. A process according to any of the preceding claims wherein the ethylene/vinyl acetate/fumaric ester interpolymer is prepared by heating ethylene under pressure with vinyl acetate and a fumaric ester in the presence of a catalyst.

8. A process according to claim 7 wherein the ethylene/vinyl acetate/fumaric ester interpolymer is prepared by heating ethylene with vinyl acetate and a fumaric ester in the presence of a catalyst at a pressure between 60 and 1500 atmospheres and at a temperature of 50—150° C.

9. A process according to either of claims 7 or 8 wherein the ethylene/vinyl acetate/fumaric ester interpolymer is prepared by heating ethylene with vinyl acetate and a fumaric ester in the presence of a catalyst at a pressure between 840 and 1000 atmospheres.

10. A process according to any of claims 7—9 wherein the catalyst is an organic peroxide.

11. A process according to any of the preceding claims wherein the ethylene/vinyl acetate/fumaric ester interpolymer is prepared at a temperature between 40° C. and 300° C.

12. A process according to claim 11 wherein the ethylene/vinyl acetate/fumaric ester interpolymer is prepared at a temperature of 65° C.

13. A process according to any of the preceding claims wherein the hydrolysis of the ethylene/vinyl acetate/fumaric ester interpolymer is accomplished under alkaline conditions.

14. A process according to claim 13 wherein an alcoholic solution of an alkali is mixed with a solution of the ethylene/

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vinyl acetate/fumaric ester interpolymers in a hydrocarbon.

15. A process according to claim 14 wherein the solution of interpolymers is 5 diluted with methanol or ethanol.

16. A process according to claim 14 wherein the alkali is sodium or potassium hydroxide.

10 17. The production of a heat hardenable interpolymers resin substantially as described hereinbefore with particular reference to the foregoing examples.

18. Heat hardenable interpolymers resins whenever produced by a process 15 claimed in any of the preceding claims.

19. The production of a moulding composition comprising an interpolymers resin claimed in claim 18 and one or more fillers by a process substantially as 20 described hereinbefore.

20. A moulding composition comprising an interpolymers resin claimed in claim 18 and a filler.

21. A process for the production of shaped articles wherein a composition 25 claimed in claim 20 is moulded at a pressure of 2000—3000 lbs./sq. in. and a temperature of substantially 150° C.

22. The production of a film from an interpolymers resin claimed in claim 18 30 using any of the solvent casting, hot casting or hot pressing methods known to the art.

23. Films and other shaped articles prepared from an interpolymers resin 35 claimed in claim 18.

Dated the 23rd day of May, 1946.

J. W. RIDSDALE,
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office by the Courier Press.—1949.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies, price 2s. 0d. each (inland) 2s. 1d. (abroad) may be obtained.

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